



Fiber Innovation Technology, Inc.

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***NOVEL PROPERTIES OF
PLA FIBERS***

by

Jeffrey S. Dugan

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Since the dawn of synthetic fiber technology, three polymers, PET, nylon, and polypropylene, have found widespread acceptance across a broad spectrum of applications, in woven, knit, and nonwoven forms, and in both apparel and industrial end-uses. Recently, poly(trimethylene terephthalate) (PTT) has been introduced and is making a bid to establish itself as a fourth broad-spectrum fiber polymer. Though the introduction of PTT is the first in decades with such potential, the even more recent introduction of poly (lactic acid) (PLA) as a commercial polymer presents textile manufacturers with perhaps an even more compelling set of properties that should prove valuable in a wide array of applications.

Polymer Characteristics

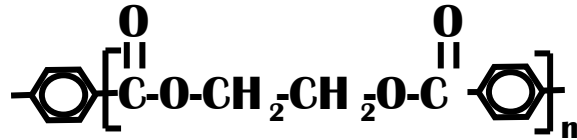
In the U.S., Cargill Dow Polymers (CDP) makes PLA by converting corn starch into lactic acid, which is then polymerized¹. Unlike other synthetic fiber materials with vegetable sources (e.g., cellulose), PLA is well suited for melt-spinning into fibers. Compared to the solvent-spinning process required for synthetic cellulosic fibers, melt spinning allows PLA fibers to be made with both lower financial cost and lower environmental cost., and allows the production of fibers with a wider range of properties.

Upon first introduction to PLA, it is tempting to note that the polymerization occurs by condensation of an acid with an alcohol, forming a polyester. The temptation in this observation is to assume that because PLA is a polyester, it will behave in many ways similarly to PET, the polymer known generically as “polyester.” Indeed, both polymers need to be dried before melting to avoid hydrolysis, both polymers readily form fibers via melt extrusion, and fibers from both polymers can be drawn (stretched) to develop useful tensile strength. Beyond these similarities, though, PLA and PET differ, sometimes only in degree, other times as polar opposites. Some differences (discussed later) arise from PLA’s vegetable source as opposed to PET’s mineral source. But significant processing and property differences arise from the differences in the respective polymer structures.

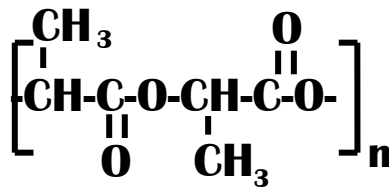
First, PET is an aromatic polyester, incorporating a benzene ring in each repeat unit. PLA, though, is an aliphatic polyester, with only relatively small pendant methyl groups to hinder rotation and to prevent easy access to the oxygen atoms in the ester linkage (see Figure 1). Second, the PET chain is nominally linear, while the PLA molecule tends to assume a helical structure. These differences allow purer grades of PLA to crystallize much more readily and, we think, to a greater extent, than PET, resulting in dramatically different processing requirements for the fiber manufacturer. These differences

sometimes present obstacles, but more often provide a greater degree of control over final fiber properties such as strength, shrinkage, and bulk.

Figure 1



PET



PLA

Unique polymer characteristics also arise from the fact that the lactide dimer occurs in three forms: the L form, which rotates polarized light in a clockwise direction, the D form, which rotates polarized light in a counter-clockwise direction, and the Meso form, which is optically inactive. During polymerization, the relative proportions of these forms can be controlled, resulting in relatively broad control over important polymer properties².

So with a thermoplastic “natural” fiber polymer, unique polymer morphologies, and control over the isomer content in the polymer, a relatively broad spectrum of properties is available to the fiber manufacturer. Below I will describe how we are employing PLA’s unique set of properties to create new possibilities in fibers and fabrics.

Sustainability

As a melt-spinnable fiber with a vegetable source, PLA has many of the advantages of both synthetic and natural fibers. Perhaps most distinctive among these, though, is the fact that, like natural fibers, its raw material is both renewable and non-polluting. This eliminates the often-underestimated problems associated with using a finite supply of oil as a raw material. Beyond having a renewable raw material, though, PLA is also compostable. After hydrolysis at 98% humidity and 60°C or higher, PLA is readily consumed by microbes³ and its component atoms are converted for possible re-use in growing more corn, beets, rice, or etc. for future conversion to PLA. Thus PLA is less environmentally costly than polymers that are recyclable, because there is a limit to the number of recycling iterations that can occur before the material loses its usefulness.

PLA is even less environmentally costly than other biodegradable thermoplastics, since the entire mass of PLA can eventually be re-converted into new PLA, whereas many other biodegradable thermoplastics incorporate at least some material derived from fossil fuels. This ability of PLA to be completely recycled at the atomic level and by natural processes is summed up in the term “sustainability.” PLA is not a perfectly sustainable polymer, since some energy must be irretrievably used in its polymerization and in converting the polymer into fibers and fabrics. But it offers superior sustainability and lower environmental impact than any other non-cellulosic synthetic fiber, and possibly even superior to some natural fibers.

Price

Sustainability and environmental impact are valuable to many manufacturers, particularly suppliers of consumer products. Traditionally, though, many of these applications would not support an increased price over less environmentally-desirable alternatives. Our initial work with PLA was done using relatively expensive polymer from Cargill Dow’s semiworks facility. But Cargill Dow now operates a large-scale production facility in Nebraska⁴ which is resulting in lower prices as commercial applications come on stream. In the past, Cargill Dow has estimated that polymer from this plant could eventually be priced “somewhere between PET and nylon”.⁵ Soon, then, a truly “environmentally friendly” fiber and fabric should be available at attractive prices.

This opens the door for PLA in such applications as diapers, wipes, and other disposable products, where compostability also offers the promise of reduced landfill space. Even more compelling commercially is the use of PLA in apparel, either at 100% or in blends with cotton. Particularly in shoe linings and activewear, the appeal to the consumer of a more environmentally-friendly product is an attractive way to enhance the product’s value, without sacrificing cost competitiveness.

Durability

If compostability is important for disposable products, and for PLA’s overall sustainability, it raises concerns of poor durability when considered for use in apparel and many other applications. In fact, though, unlike some other biodegradable polymers, PLA has very good durability in most applications. While some biodegradable polymers are available to consumption by microbes as soon as the microbes encounter the polymer, PLA is not biodegradable in its “as-extruded” state. Instead, it must first be hydrolyzed before it becomes biodegradable. To achieve hydrolysis of PLA at significant levels, both a relative humidity at or above 98% and a temperature at or above 60°C are required⁶. Once these conditions are met, degradation occurs rapidly⁷, but it is easy to see that for most applications, durability concerns should not be an issue for PLA.

Hydrophilicity

While PLA is attractive in activewear because of the environmental consciousness of the targeted consumer, it is also well suited to inclusion in more conventional apparel because of its hydrophilicity. Because water molecules have access to the polar oxygen linkages in the PLA molecule, it has a higher natural hydrophilicity than most other thermoplastic polymers, including polypropylene, nylon, and PET. This improves the wettability of the fiber as well as the moisture vapor transmission of fabrics made with PLA fibers, which allows improvements in “breathability” of garments such as shirts, dresses, underwear, and shoes. PLA fibers are not as wettable as cotton, but they can provide moisture transport improvements when they replace fibers like PET or nylon.

PLA’s hydrophilicity can also be of use in applications where much higher moisture transport rates are required. The most effective moisture transport fiber available today is the “4DG” fiber with a cross section incorporating multiple deep grooves that provide capillary wicking (illustrated in Figure 2). This fiber is often made from PET, with a hydrophilic finish on the fiber’s surface to allow the wicking to take place (water will not fill grooves whose surface comprises hydrophobic PET). As water is transported along these grooves, some of the finish is typically emulsified in the water. As the finish concentration in the water increases, the surface tension of the water decreases, thus reducing the driving force for the capillary wicking. Further, after repeated exposure to water, much of the finish may ultimately be washed away from the fiber, further degrading performance. This can be corrected using a permanent finish, but if we make the fiber from PLA, we have a degree of built-in, permanent hydrophilicity, so our reliance on topical finishes is reduced.

Figure 2



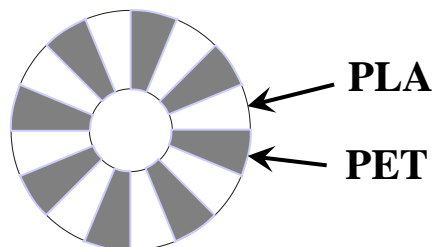
Finally, enhanced hydrophilicity can also be of use in the formation of some nonwoven fabrics. In hydroentanglement, a more hydrophilic fiber surface improves the “grip” of the water jets on the fiber, which results in a higher degree of entanglement, other parameters being kept constant. And in the formation of wet-laid fabrics, an inherently hydrophilic fiber gives easier and more uniform dispersion than a hydrophobic fiber.

Dyeability

Also important to its use in various apparel applications is PLA's dyeability. It can be disperse-dyed using standard PET dyes and dyeing procedure, but again there is a difference between PLA and PET. PLA's refractive index is lower than that of PET or nylon, so it can be dyed to deeper and brighter shades.

Dyeability is admittedly of greater concern for knit or woven fabrics than for nonwovens, but there are nonwoven segments where dyeability is important. One of these is the manufacture of synthetic suedes and leathers. These fabrics are most commonly made starting with splittable segmented fibers that can be carded into a loose web that is then hydroentangled to simultaneously entangle the fibers and to split them into their multiple individual segments. Though the beginning fibers have the strength, processability, and some of the production efficiencies of, say, 3 denier per filament (dpf) fibers, the resulting fabric contains fibers below 0.2 dpf. With the proper fabric finishing, these fine fibers are well suited to mimicking the feel of suede or leather. One advantage of these synthetic suedes and leathers over natural products is that they are naturally white and can be dyed to lighter and purer shades than natural skins. Traditionally, the splittable segmented fibers used in these fabrics are made from alternating segments of PET and nylon. Because these two polymers do not dye with the same dyes, a uniform shade must be achieved with separate dyeings and dyestuffs. Making a segmented fiber entirely of nylon or entirely of PET is not an option because the adjacent segments have a high degree of cohesion and will not split apart in hydroentangling. But a splittable segmented fiber made of alternating segments of PET and PLA (Figure 3) will split apart and can be dyed in a single step with a single set of dyestuffs, improving the efficiency and the uniformity of the dyeing.

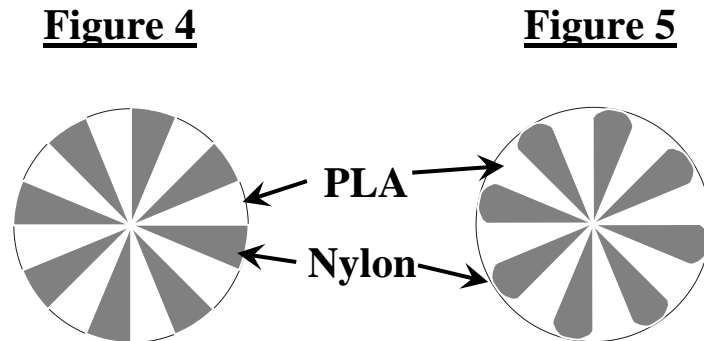
Figure 3



Resilience

Another useful property of PLA in fabrics made from splittable fibers is its resilience. After splitting, the individual segments are so small that some fabric bulk is lost compared to similar weight fabrics made with higher-denier fibers. In cases where this bulk is important, the PET (which is less resilient than nylon) in a PET/nylon splittable fiber can be replaced by PLA (Figure 4), which is highly resilient and can recapture some

of the lost bulk. A common difficulty in forming hydroentangled fabrics from nylon/PET or nylon /PLA splittable fibers is that if the fiber is made to be easily-split in hydroentangling, it is likely to split undesirably in carding. And such fibers made to resist splitting in carding are unlikely to split easily in hydroentangling. Using proprietary FIT spinning technology, we have created a segmented fiber cross section (Figure 5) that effectively resists splitting without preventing splitting in the hydroentangling step.



But PLA’s resilience is also high enough to be attractive in high-loft applications such as fiberfill insulation, pillows, and mattress tops. For these applications, an undesirable fiber scroopiness that is also a property of PLA (and will be discussed later) must be eliminated, but this can be done with the proper fiber finishes. Finally, PLA is being tested as a carpet fiber, but these tests are incomplete at the time of this writing.

Because PLA is unlikely to be as inexpensive as current polypropylene prices even upon full commercialization, we have created a fiber cross section that reduces total raw materials cost without sacrificing a significant amount of resilience. One way to do this is to form a fiber with a core of polypropylene (PP) with a sheath of PLA. But if the PP core is instead split into three separate cores, as in Figure 6, the resulting PLA structure connects the fiber’s sheath with the center via the three “spokes.” This structure is a much more rigid and resilient structure than the hollow “pipe” of the sheath/core fiber. Again using our proprietary spinning technology, we have refined the three-core cross section for even better economics without sacrificing performance. In Figure 6, you can see that if the PP content of the fiber is increased, the PLA spokes get thinner until the PP cores join and the PLA sheath is no longer reinforced by its connection to the fiber’s center. But with the optimized cross section shown in figure 7, the PP content (and thus the reduction of polymer cost) can be maximized while the highly-resilient PLA structure is maintained.

Figure 6

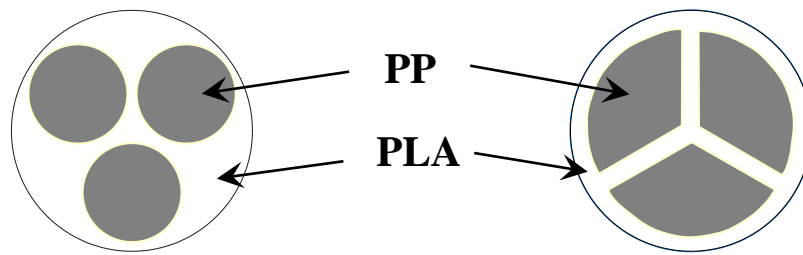
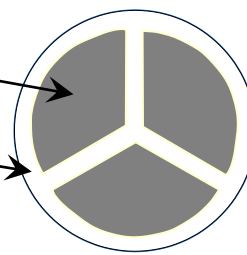


Figure 7



Flame Properties

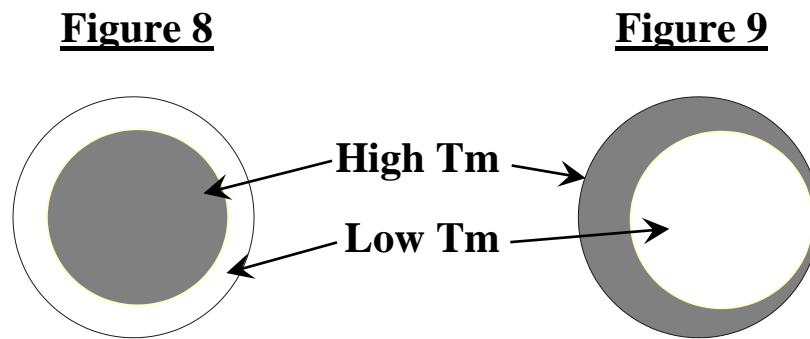
But resilience is not the only appealing PLA property for most high-loft applications. Its flammability characteristics are also more benign than those of un-filled or un-treated PET. That is not to say that PLA fibers are inherently flame-proof. They will burn, but when they do, they release significantly less visible smoke than is common with other non-FR materials, so visibility hazards in a fire are reduced. Further, the peak energy release rate of burning PLA is less than 60% that of PET⁸. So, especially in combination with other FR materials, PLA fires are less likely to spread to adjacent articles. Finally, once heated above its heat-set temperature, a PLA fiber has a very high shrink force, so in flame-protection models that rely on the material to shrink away from the flame, PLA fabrics should prove superior. For total protection, some FR treatment will probably be necessary for PLA, but because of the properties listed above, it is likely that lower levels, or less costly FR materials can be used compared to those used to treat PET. In addition to high-loft applications, PLA's burning properties also make PLA fibers attractive for use in upholstery, upholstery backings, and other furniture fabrics, as well as window dressings such as drapes, linings, and pleated blinds.

Melt Temperature Versatility

One of the more intriguing results of the ability to polymerize PLA with control over the content and arrangement of the three stereoisomers is that the polymer's melt temperature can be controlled between about 120°C and 175°C. One valuable use of this ability is to manufacture bicomponent binder fibers, with a high-melting PLA core in a sheath of a low-melting grade (Figure 8). These fibers perform similarly to standard polyethylene/PET or coPET/PET binder fibers, with the added advantage that the entire binder fiber has the high sustainability features of PLA. If the other fibers in the fabric (non-binder fibers) are also PLA, or another natural or cellulosic fiber, then the entire fabric can be composted. This is not the case with any other binder fiber of which I am aware.

Similarly, PLA grades with differing melt temperatures also have different degrees of crystallinity (note that the grades with low "melt" temperatures are actually fully

amorphous, and the temperature referred to as a melt temperature is actually the center of a range at which the polymer begins to flow at useful rates). This means that we can make a self-crimping (also known as self-texturing or self-bulking) fiber by co-extruding a low-melting grade with a high-melting grade in a side-by-side or eccentric sheath/core cross section (Figure 9). After drawing and heat-setting, heating this fiber above its heat-set temperature will cause the fiber to shrink. Since the two polymer grades will have different shrinkage rates, the fiber will curl into a helical shape, providing bulk. As with the all-PLA binder fiber above, this fiber achieves self-bulking without the introduction of a material that cannot be composted, or which reduces the overall sustainability of the fabric.



Other Attractive Properties

As if the properties discussed above were not impressive enough, PLA is also highly resistant to degradation by ultraviolet radiation, with no loss in elongation after 100 hours in Xenon arc testing⁹, and minimal losses at longer exposure. Amazingly for a polymer that is readily consumed by microbes in composting, PLA does not support bacterial growth before composting. Finally, PLA's specific gravity is only 1.25. Since this is less than that of PET, and since fibers are sold by the pound and converted into fabrics sold by length or area, PLA fibers can replace PET with no increase in cost, even if PLA fibers are priced 12 percent higher.

Drawbacks

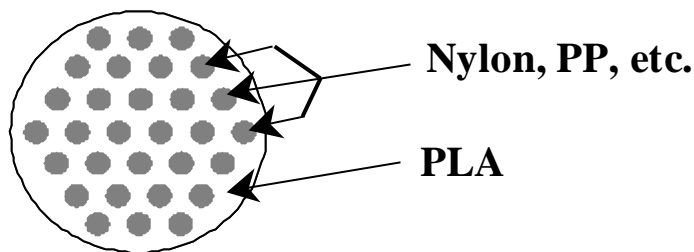
Of course, no material has only useful and valuable properties. But those properties of PLA which could be called drawbacks are relatively few, and some are even useful for certain applications.

The one property for which we have not found a promising application is PLA's relatively poor abrasion resistance. This may limit or even preclude the use of PLA fibers in some high-performance apparel applications, in ropes, or in other uses where abrasion resistance is required. But in tests to date, it has not proven severe enough to limit the usefulness of PLA fibers in carpet.

A second “drawback” is PLA’s relatively low melt temperature. Even the most crystalline form melts at about 175°C. This will limit PLA’s applicability in high-temperature environments, but it is at least high enough not to preclude ironing and drying in apparel applications. Further, Cargill Dow reports that a blend of optically-pure polymers of opposite rotation forms an “interlocking” morphology with a crystalline melt temperature above 210°C¹⁰. We have not yet tested this polymer in fiber form, but if it can be easily extruded and processed, it should remove most concerns regarding the use of PLA fibers at relatively high temperatures.

I mentioned above that PLA requires both high humidity and high temperature to be hydrolyzed. For most applications, these conditions are fairly extreme. But in environments where hydrolysis is a problem for PET, it is a more severe problem for PLA. And in some applications where PET’s hydrolysis resistance is acceptable, PLA’s lower resistance may render it unsuitable. However, there is at least one application for which this property is actually useful. Figure 10 illustrates a bicomponent “islands/sea” cross section, which is used to produce microfiber fabrics. An insoluble polymer is extruded in many “islands” in a “sea” of a soluble polymer. This allows the production and handling of a standard size fiber, until the fabric has been formed. Then the fabric is passed through a bath of solvent to remove the sea polymer, liberating the islands as individual filaments and producing a fabric made of microfibers. In the past, organic solvents have been used to remove a sea of polystyrene, but of course, there are environmental and flammability concerns associated with the use of organic solvents. Sea polymers soluble in hot water have been used¹¹, but these are expensive, and become tacky when moisture is absorbed from aqueous fiber finishes or from the air. But if PLA is used as a sea polymer, it can be easily removed with 3 minutes exposure in a bath of hot, 3% caustic, conditions similar to those used in commercial bleaching and scouring operations. With this approach, a fabric made with 3 denier per filament (dpf) staple fibers can be simply and cost-effectively converted into a fabric with 0.6 dpf fibers, ideal for filtration, technical wipes, and synthetic leather.

Figure 10



Finally, PLA has a surface cohesion that gives the fibers a property known as “scoop.” This is the property of fibers like wool that causes a “crunchiness” to be felt when the fibers are rubbed against one another, presumably caused by a stick-slip action as the fibers slide past each other. Untreated PLA fibers have sufficient scoop to resist the recovery of a high-loft web after deformation, potentially threatening the use of PLA’s resilience in many applications. This can be entirely overcome, though, with the use of

the right fiber finishes. And in other applications, it can even be desirable. One such application, for instance, is in blends with wool. Because PLA has this scroop, it can be used to extend wool at low cost and without sacrificing the natural feel of the wool. In needlepunching, the tendency of the fibers to resist sliding past one another makes needlepunched fabrics stronger and more resistant to creep. And in spun yarns, the same tendency can produce remarkably high strength.

The Future

As you can see, we've only begun to develop applications for the unique property set offered by PLA fibers. Many more applications are likely to arise just from the properties discussed above. But there is also still quite a bit we have not yet investigated regarding the properties of the polymer and fibers made from it. With future discoveries in polymer and fiber properties and future developments in appropriate applications for the fibers, we expect the use of PLA fibers to expand rapidly in the next several years. It seems likely that, as it matures, PLA will eventually find acceptance in an array of applications as broad as PET, nylon, and polypropylene.

Acknowledgments

It is beyond the scope of this paper to list all those who have contributed to the developments listed. But immediate and invaluable input has been provided by Cargill Dow Polymers, LLC, and Fiber Innovation Technology employees Garland Earley, Frank Harris, Mike Hodge, Gus Meyer, Chris Parris, and John Wilson, and is gratefully acknowledged.

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